PROCESS AND APPARATUS FOR GROWING A CRYSTALLINE GALLIUM-CONTAINING NITRIDE USING AN AZIDE MINERALIZER

CROSS-REFERENCES TO RELATED APPLICATIONS

This application claims priority to U.S. Provisional Application 61/086,799, filed on Aug. 7, 2008, commonly assigned, and of which is incorporated by reference in its entirety for all purposes hereby.

STATEMENT AS TO RIGHTS TO INVENTIONS MADE UNDER FEDERALLY SPONSORED RESEARCH AND DEVELOPMENT

Not Applicable

REFERENCE TO A "SEQUENCE LISTING," A TABLE, OR A COMPUTER PROGRAM LISTING APPENDIX SUBMITTED ON A COMPACT DISK

Not Applicable

BACKGROUND OF THE INVENTION

The present invention generally relates to processing of materials for growth of crystals. More particularly, the present invention provides a method for obtaining a gallium-containing nitride crystal by an ammonobasic or ammonoacidic technique, but there can be others. In other embodiments, the present invention provides an apparatus for large scale processing of nitride crystals, but it would be recognized that other crystals and materials can also be processed. Such crystals and materials include, but are not limited to, GaN, AlN, InN, InGaN, AlGaN, and AlInGaN, and others for manufacture of bulk or patterned substrates. Such bulk or patterned substrates can be used for a variety of applications including optoelectronic devices, lasers, light emitting diodes, solar cells, photoelectrochemical water splitting and hydrogen, photodetectors, integrated circuits, and transistors, among other devices.

Gallium nitride containing crystalline materials serve as a starting point for manufacture of conventional optoelectronic devices, such as blue light emitting diodes and lasers. Such optoelectronic devices have been commonly manufactured on sapphire or silicon carbide substrates that differ from the deposited nitride layers. In the conventional Metallo-Organic Chemical Vapor Deposition (MOCVD) method, deposition of GaN is performed from ammonia and organometallic compounds in the gas phase. Although successful, conventional growth rates achieved make it difficult to provide a bulk layer of GaN material. Additionally, dislocation densities are also high and lead to poorer optoelectronic device performance.

Other techniques have been proposed for obtaining bulk monocrystalline gallium nitride. Such techniques include use of epitaxial deposition employing halides and hydrides in a vapor phase and is called Hydride Vapor Phase Epitaxy (HVPE) ["Growth and characterization of freestanding GaN substrates," K. Motoki et al., Journal of Crystal Growth 237-239, 912 (2002)]. Unfortunately, drawbacks exist with HVPE techniques. In some cases, the quality of the bulk monocrystalline gallium nitride is not generally sufficient for high quality laser diodes because of issues with dislocation density, stress, and the like.

Techniques using supercritical ammonia have been proposed. Peters has described the ammonothermal synthesis of aluminium nitride [J. Cryst. Growth 104, 411 418 (1990)]. R. Dwiliński, et al. have shown, in particular, that it is possible to obtain a fine-crystalline gallium nitride by a synthesis from gallium and ammonia, provided that the latter contains alkali metal amides (KNH_2 or $LiNH_2$). These and other techniques have been described in "AMMONO method of BN, AlN, and GaN synthesis and crystal growth", Proc. EGW-3, Warsaw, Jun. 22 24, 1998, MRS Internet Journal of Nitride Semiconductor Research, Http://nsr.mij.mrs.org/3/25, "Crystal growth of gallium nitride in supercritical ammonia" J. W. Kolis, et al., J. Cryst. Growth 222, 431 434 (2001), and Mat. Res. Soc. Symp. Proc. Vol. 495, 367 372 (1998) by J. W. Kolis, et al. However, using these supercritical ammonia processes, no wide scale production of bulk monocrystalline was achieved.

Dwiliński, in U.S. Pat. Nos. 6,656,615, 7,160,388, and 7,335,262, and D'Evelyn, in U.S. Pat. Nos. 7,078,731 and 7,101,433, which are hereby incorporated by reference in their entirety, generally describe apparatus and methods for ammonothermal crystal growth of GaN. These conventional methods are useful for growth of relatively small GaN crystals but have limitations for large scale manufacturing. For example, apparatus with an inner diameter of 40 mm is somewhat useful for growing **1"** diameter GaN crystals but is generally not suitable for large scale growth of crystals. Other autoclave related techniques are described in U.S. Pat. Nos. 3,245,760, 2,607,108, and 4,030,966. Although somewhat successful, drawbacks exist with these conventional ammonothermal techniques.

From the above, it is seen that improved techniques for crystal growth are highly desired.

BRIEF SUMMARY OF THE INVENTION

According to the present invention, techniques related to processing of materials for the growth of crystal are provided. More particularly, the present invention provides a method for obtaining a gallium-containing nitride crystal by an ammonobasic or ammonoacidic technique, but there can be others. In other embodiments, the present invention provides an apparatus for large scale processing of nitride crystals, but it would be recognized that other crystals and materials can also be processed. Such crystals and materials include, but are not limited to, GaN, AlN, InN, InGaN, AlGaN, and AlInGaN, and others for manufacture of bulk or patterned substrates. Such bulk or patterned substrates can be used for a variety of applications including optoelectronic devices, lasers, light emitting diodes, solar cells, photoelectrochemical water splitting and hydrogen generation, photodetectors, integrated circuits, and transistors, among other devices.

In a specific embodiment, the present invention provides an apparatus and method for large-scale manufacturing of gallium nitride. In a specific embodiment, the present apparatus comprises a large diameter autoclave and a raw material basket. Methods include metered addition of one or more dopants in the raw material and control of atmosphere during crystal growth. The apparatus and methods are scalable up to very large volumes and are cost effective.

In a specific embodiment, the present invention provides a process for growing a crystalline gallium-containing nitride, e.g., GaN. The process includes providing a high pressure apparatus comprising gallium-containing feedstock in one zone, at least one seed in another zone, an azide mineralizer, and at least one metal. In a specific embodiment, the azide mineralizer and the metal are provided in a predetermined ratio such that nitrogen generated by decomposition of the azide mineralizer and hydrogen generated by reaction of the